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Carlos Frontera, José Luis García-Muñoz, and Oscar Castaño

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Influence of *R*-ion size on spin state of Co and magnetic properties of $RBaCo_2O_{5.50}$ cobaltites

Carlos Frontera,[a] José Luis García-Muñoz, and Oscar Castaño[b]
Institut de Ciència de Materials de Barcelona, CSIC, Campus Universitari de Bellaterra, E-08193 Bellaterra, Spain

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This work presents a comparative magnetic study of $PrBaCo_2O_{5.50}$ and $YBaCo_2O_{5.50}$. Samples studied have been carefully prepared, specially the $PrBaCo_2O_{5.50}$ one, to avoid the formation of oxygen vacancy disorder. High temperature magnetic measurements indicate different spin states of Co ions in both compounds. Neutron powder diffraction below RT indicate a different succession of magnetic arrangements. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2829747]

I. INTRODUCTION

Due to their remarkable properties, cobalt oxides represent one of the most promising research topics in the field of strongly correlated electron materials. Of special interest is the facility shown by Co ions (especially in perovskitelike structures) to adopt different spin states. This additional degree of freedom, quenched in other transition metal oxides, is strongly coupled with lattice, magnetic, and transport properties. In this context, remarkable research efforts are aimed to explore and to understand the challenging properties of layered cobaltites of the type $RBaCo_2O_{5+\delta}$ (R=rare earth), with $0 \leqslant \delta \leqslant 1$ and a highly ordered structure. These compounds present remarkable physical properties: giant magnetoresistance, large thermoelectric power, metal-insulator (MI) transitions, high oxygen mobility, sharp spin state (SS) transitions, etc.[1–11]

Besides the obvious role of oxygen content, controlling not only the mean valence of Co ions but also its coordination environment (pyramidal or octahedral), much less studied is the role of the size of the rare earth R. Emerging interest has been centered on $RBaCo_2O_{5.50}$ compounds during the past years (presenting only Co^{3+}) as they present intriguing transport and magnetic properties: a MI transition (accompanied by SS transitions), successive magnetic transitions, large thermoelectric power, etc.[2,5,6,10–12] In this case (δ=0.5), it is well established that oxygen vacancies order forming filled and empty rows of oxygen sites along a in the RO_δ-planes. Associated with this ordering, intermediate spin (IS)/low spin (LS) Co^{3+} states were found for $GdBaCo_2O_{5.50}$ to be orderly distributed in the structure below T_{MI} (IS/high spin (HS) states above the SS transition at T_{MI}).[6] This means that the SS transition takes place in an ordered manner (as was also suggested in Ref. 1).

In spite of the picture drawn in several papers, the low temperature ordered magnetic structure, studied by neutron diffraction, on $NdBaCo_2O_{5.50}$ suggested that half of the octahedral Co^{3+} ions are in an IS state (Ref. 7), in apparent contradiction with results on $GdBaCo_2O_{5.50}$. This opens the possibility of a dependence of spin state of cobalt on the size of the rare earth (the size of Nd is considerably larger than that of Gd). Such a dependence could be understood by considering the effect of rare earth size on the structure that governs the crystal field. To study this dependence, it must be taken into account that for large rare earths, due to the preparation conditions, the order between oxygen ions and oxygen vacancies can be partially lost, thus introducing undesirable side effects affecting the comparison.[13,14] In this paper, we present a comparative study, based on magnetic measurements and neutron powder diffraction, of the magnetic properties of $PrBaCo_2O_{5.50}$ ($R_{Pr} \cong 1.18$ Å) and $YBaCo_2O_{5.50}$ ($R_Y \cong 1.08$ Å), intended to gain some insight on the role of R-size in $RBaCo_2O_{5.50}$ cobaltites. We have taken special care in the $PrBaCo_2O_{5.50}$ preparation to obtain a well ordered sample.

II. EXPERIMENTAL

Initial $PrBaCo_2O_{5+\delta}$ and $YBaCo_2O_{5+\delta}$ samples were prepared by sol-gel methods. Praseodymium or yttrium acetate hydrate (Strem Chemicals, Inc., and Alfa Aesar, respectively), barium acetate, and cobalt acetate tetrahydrate (Alfa Aesar) were dissolved in the suitable stoichiometric ratio in distilled water at 60 °C for a few minutes. Then, an excess of citric acid monohydrate (Sigma-Aldrich) was added to the solution until saturation (~70 g of citric acid for 15 g of the sample). The mix was held at 110 °C under vigorous stirring in order to evaporate the water solvent and the resultant acetic acid. The final product was a dark violet gel, which was thermally fired at 550 °C in a muffle furnace for 5 h in order to eliminate the organic material. The black powder obtained was pressed into pellets at 10 tons and calcined in a tubular furnace under air at 1075 °C for 80 h for $PrBaCo_2O_{5+\delta}$ and at 1050 °C for 24 h for $YBaCo_2O_{5+\delta}$. The bars were then cooled slowly (−60 °C/h) to RT. X-ray powder diffraction (XRD) data show that initial compounds were well crystallized and free from impurities up to the detection limit of the technique (1 wt %).

To reduce the as prepared $PrBaCo_2O_{5+\delta}$ sample (with $\delta \simeq 0.75$) to $\delta \simeq 0.50$, getting an optimal vacancy ordering, we

[a]Electronic mail: frontera@icmab.es.
[b]Present address: Institut de Bioenginyeria de Catalunya C/Baldiri Reixac 13, 08028 Barcelona, Spain.

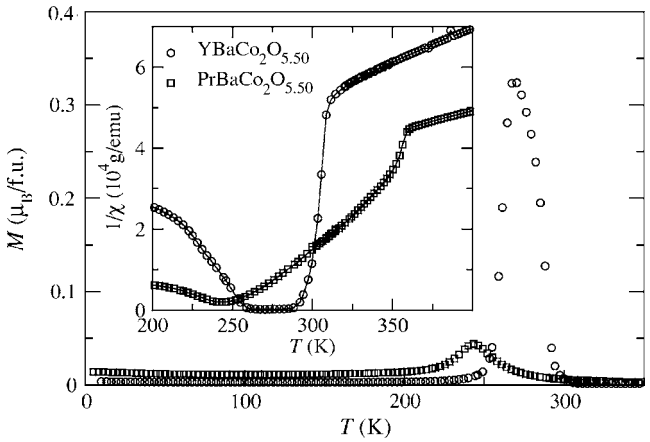

FIG. 1. Zero-field-cooled and field-cooled magnetization of $PrBaCo_2O_{5.50}$ (□) and $YBaCo_2O_{5.50}$ (○) measured under $\mu_0 H=0.1$ T. The inset shows the inverse susceptibility.

introduced the as prepared $PrBaCo_2O_{5+\delta}$ powder in a Pyrex-glass ampoule together with a large amount of metallic Cu. We sealed the ampoule, annealed it at 460 °C for 180 h, and then slowly cooled it (−3 °C/h) down to RT. The obtained compound were characterized by means of XRD and found to be well crystallized and free from impurities. The refinement of XRD data rendered the well known $a_p \times 2a_p \times 2a_p$ cell, with a volume per Co ion of $V/\text{Co ion} \simeq 58.55$ Å^3. According to Table I in Ref. 15, this corresponds to an oxygen content above $\delta=0.46$ ($V/\text{Co} \simeq 58.58$ Å^3) and near $\delta=0.50$ ($V/\text{Co} \simeq 58.53$ Å^3).

To correct the oxygen stoichiometry of the sintered $YBaCo_2O_{5+\delta}$ sample, we annealed it, in powder form, under oxygen atmosphere at 290 °C for 40 h and slowly cooled it to RT at 5 °C/h. XRD showed a well crystallized and impurity-free (up to the detection limit) sample. Cell parameters obtained (also rendering a $a_p \times 2a_p \times 2a_p$ cell) coincide with those previously reported.[16]

Further structural studies have been carried out using neutron powder diffraction (NPD) on different beamlines at ILL (D2B, λ=1.594 Å; D1B, λ=2.52 Å), at different temperatures between 5 K and RT, and using synchrotron x-ray powder diffraction (SXRPD) at the ID31 beamline of ESRF (Grenoble, France). A short wavelength λ=0.399 78(25) Å, to reduce the absorption, was selected with a double-crystal Ge (111) monochromator and calibrated with Si NIST (a =5.430 94 Å). Optimum transmission was achieved by enclosing the finely grounded sample in a 0.5 mm diameter borosilicate glass capillary and by appropriately spinning the capillary in the beam ensured for a good powder averaging. Diffraction data have been analyzed with the Rietveld method using the FULLPROF suite of programs.[17] The joint refinement of RT NPD and SXRPD data confirmed the $a_p \times 2a_p \times 2a_p$ cell found by x ray for both compounds, the oxygen content ($\delta \simeq 0.50$) and the well ordered distribution of oxygen vacancies within RO_δ planes (R=Pr and Y).

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature evolution of the magnetization of $PrBaCo_2O_{5.50}$ and $YBaCo_2O_{5.50}$ (measured using a Quantum Design commercial superconducting quantum interference device under an applied field of 0.1 T). Magnetization curves of both compounds are characterized by the appearance, on cooling, of a ferromagnetic (FM) signal, followed by its sudden disappearance. Important differences between the two curves must be remarked. First, the ferromagnetic signal measured under an applied field of 0.1 T in the $YBaCo_2O_{5.50}$ compound is much larger ($\sim 0.33 \mu_B$/f.u.). than that for $PrBaCo_2O_{5.50}$ ($\sim 0.04 \mu_B$/f.u.). Second, the disappearance of the ferromagnetic moment (on cooling) is more sudden in $YBaCo_2O_{5.50}$ than in $PrBaCo_2O_{5.50}$. Last, the transition temperatures are shifted down in $PrBaCo_2O_{5.50}$. As in previous works, we will refer to the first transition temperature as T_{N_1} [defined as the point where $M(T)$ curve displays an inflection point]. Neutron powder diffraction measurements show that this FM moment comes from a canted antiferromagnetic (AFM) structure.[13,18] We will refer to the second transition point as T_{N_2}, defined as the point where the magnetization displays a maximum. With these definitions, it is found that $T_{N_1} \simeq 287$ and 250 K, and $T_{N_2} \simeq 270$ and 242 K for $YBaCo_2O_{5.50}$ and $PrBaCo_2O_{5.50}$, respectively.

Differences in the behavior of the inverse susceptibility (inset of Fig. 1) are also very revealing. $PrBaCo_2O_{5.50}$ shows a transition in the paramagnetic state (above T_{N_1}), at about $T_{\text{MI}} \simeq 360$ K, characterized by a sudden change in the slope of the $\chi^{-1}(T)$ curve. This transition is present in most $RBaCo_2O_{5.50}$ compounds and corresponds to a partial SS transition of Co ions,[2,6] which is accompanied by a MI transition, a structural transition, and a large calorimetric signal.[7,19] Remarkably, in $YBaCo_2O_{5.50}$, the MI and structural transitions (also accompanied by a large calorimetric signal) take place at T_{N_1}.[16] Consequently, the change in the slope of the inverse susceptibility in the paramagnetic region does not occur. A remarkable difference in this high temperature region concerns the slope of the $\chi^{-1}(T)$ curve: It is higher for $YBaCo_2O_{5.50}$ than for $PrBaCo_2O_{5.50}$. This indicates a larger effective paramagnetic moment in $PrBaCo_2O_{5.50}$. By fitting a Curie law for $T > T_{\text{MI}}$, we obtain $\mu_{\text{eff}}=4.58 \mu_B$/f.u. (Y) and $\mu_{\text{eff}}=5.91 \mu_B$/f.u. (Pr). From this, it is apparent that the spin state of Co^{3+} above T_{MI} is different in Y and in Pr. From μ_{eff}, above T_{MI}, Co^{3+} ions would be in a 1:1 mixture of HS and IS states in $PrBaCo_2O_{5.50}$ (expected $\mu_{\text{eff}}=5.65 \mu_B$/f.u.), but for Y the obtained value is nearer to that expected for all Co ions in IS ($\mu_{\text{eff}}=4.0 \mu_B$/f.u.).

Low temperature NPD patterns reveal the appearance of several magnetic peaks in both compounds. As found in previous works, these peaks can be indexed by means of a magnetic cell doubling a and c lattice parameters in both cases.[7,13,18] Figure 2 shows the thermal evolution of the integrated intensity of the most prominent magnetic peaks. In $YBaCo_2O_{5.50}$, it can be clearly seen that at T_{N_1}, on cooling, a $(\frac{1}{2}\ 1\ 1)$ magnetic peak appears. This implies the appearance of an antiferromagnetic structure doubling a lattice parameter. At T_{N_2}, the $(\frac{1}{2}\ 1\ 1)$ reflection vanishes (on cooling), and new magnetic reflections appear. From the indices in Fig. 2, the AFM structure below T_{N_2} doubles also the c lattice parameter. In accordance with previous results in $TbBaCo_2O_{5.50}$,[18] below T_{N_2} (at T_{N_3}) a third magnetic transi-

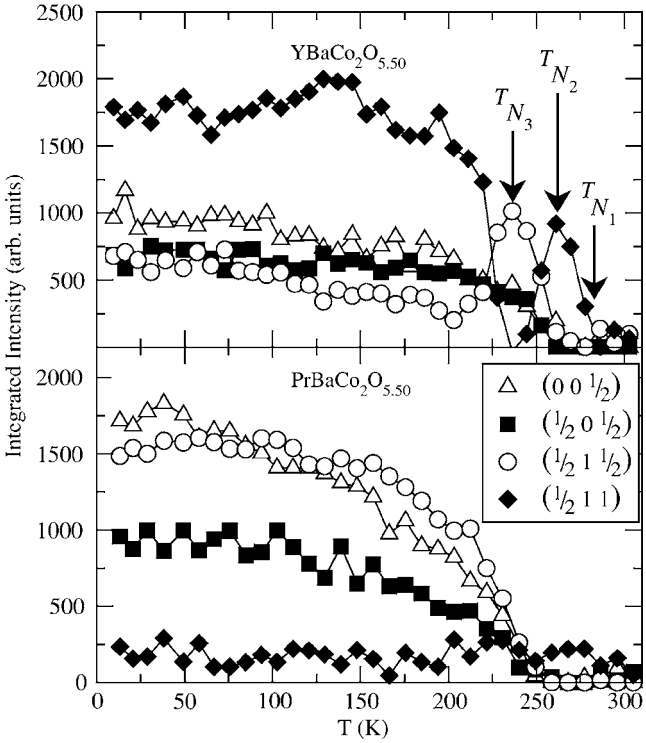

FIG. 2. Thermal evolution of the integrated intensity in the most intense magnetic peaks for (a) $YBaCo_2O_{5.50}$ and (b) $PrBaCo_2O_{5.50}$. Indices correspond to the $a_p \times 2a_p \times 2a_p$ structural lattice.

tion takes place. This transition is evidenced in Fig. 2 by a sudden shrink of $(\frac{1}{2}\ 1\ \frac{1}{2})$ and the reappearance of $(\frac{1}{2}\ 1\ 1)$ magnetic peaks.

For $PrBaCo_2O_{5.50}$, no significant variation of the $(\frac{1}{2}\ 1\ 1)$ peak can be seen around T_{N_1}. This contrasts with the results previously published for a $PrBaCo_2O_{5.50}$ sample presenting a significant fraction of oxygen-vacancy disorder.[13] In that case, a significant variation of this diffraction peak can be clearly appreciated. This difference can be ascribed to this disorder.[14] In any case, in view of the small magnetic signal found for $PrBaCo_2O_{5.50}$, a small variation of this peak (below data noise) cannot be discarded. At T_{N_2}, clear magnetic reflections appear. As for $YBaCo_2O_{5.50}$, they can be indexed by doubling a and c lattice parameters. Below T_{N_2}, data plotted in Fig. 2(b) show a smooth behavior, and no further magnetic transition can be appreciated.

IV. SUMMARY AND CONCLUSIONS

In summary, we have sintered and studied two samples of $YBaCo_2O_{5.50}$ and $PrBaCo_2O_{5.50}$ compounds, presenting both a very high degree of oxygen order. Magnetic measurements indicate that at high temperature (above T_{MI}), they present different spin states. In this case, we have found that the values of μ_{eff} obtained by fitting a Curie law to $\chi^{-1}(T)$ curves indicate a 1:1 mixture of IS and HS in $PrBaCo_2O_{5.50}$, but, for $YBaCo_2O_{5.50}$, a uniform IS state is more likely.

On cooling, the FM signal found in $YBaCo_2O_{5.50}$ is much higher than that of $PrBaCo_2O_{5.50}$. Accompanying this transition, at T_{N_1}, the $(\frac{1}{2}\ 1\ 1)$ magnetic peak emerges in $YBaCo_2O_{5.50}$ although no significant variance is seen in $PrBaCo_2O_{5.50}$. On further cooling, at T_{N_2}, new magnetic peaks appear in both compounds. Below this point, at T_{N_3}, $YBaCo_2O_{5.50}$ presents a third transition, as happens in $TbBaCo_2O_{5.50}$.[18] This transition is absent for higher-size rare earths such as Pr or Nd. Further investigations to identify the mechanisms driving these differences are needed.

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[1] I. O. Troyanchuk, N. V. Kasper, D. D. Khalyavin, H. Szymczak, R. Szymczak, and M. Baran, Phys. Rev. Lett. **80**, 3380 (1998).
[2] A. Maignan, C. Martin, D. Pelloquin, N. Nguyen, and B. Raveau, J. Solid State Chem. **142**, 247 (1999).
[3] E. Suard, F. Fauth, V. Caignaert, I. Mirebeau, G. Baldinozzi, Phys. Rev. B **61**, R11871 (2000).
[4] Y. Moritomo, T. Akimoto, M. Takeo, A. Machida, E. Nishibori, M. Takata, M. Sakata, K. Ohoyama, and A. Nakamura, Phys. Rev. B **61**, R13325 (2000).
[5] M. Respaud, C. Frontera, J. L. García-Muñoz, M. A. G. Aranda, B. Raquet, J. M. Broto, H. Rakoto, M. Goiran, A. Llobet, and J. Rodríguez-Carvajal, Phys. Rev. B **64**, 214401 (2001).
[6] C. Frontera, J. L. García-Muñoz, A. Llobet, and M. A. G. Aranda, Phys. Rev. B **65**, 180405(R) (2002).
[7] F. Fauth, E. Suard, V. Caignaert, and I. Mirebeau, Phys. Rev. B **66**, 184421 (2002).
[8] J. C. Burley, J. F. Mitchell, S. Short, D. Miller, and Y. Tang, J. Solid State Chem. **170**, 339 (2003).
[9] A. A. Taskin, A. N. Lavrov, and Y. Ando, Proceedings of the 22nd International Conference on Thermoelectrics 2003, p. 196.
[10] A. A. Taskin, A. N. Lavrov, and Y. Ando, Phys. Rev. Lett. **90**, 227201 (2003).
[11] D. D. Khalyavin, S. N. Barilo, S. V. Shiryaev, G. L. Bychkov, I. O. Troyanchuk, A. Furrer, P. Allenspach, H. Szymczak, and R. Szymczak, Phys. Rev. B **67**, 214421 (2003).
[12] A. Maignan, V. Caignaert, B. Raveau, D. Khomskii, and G. Sawatzky, Phys. Rev. Lett. **93**, 026401 (2004).
[13] C. Frontera, J. L. García-Muñoz, A. E. Carrillo, M. A. G. Aranda, I. Margiolaki, and A. Caneiro, Phys. Rev. B **74**, 054406 (2006).
[14] C. Frontera, J. L. García-Muñoz, O. Castaño, C. Ritter, and A. Caneiro, "Effect of oxygen disorder on magnetic properties of $PrBaCo_2O_{5.50}$ layered cobaltite," J. Phys.: Condens. Matter (in press).
[15] S. Streule, A. Podlesnyak, J. Mesot, M. Medarde, K. Conder, E. Pomjakushina, E. Mitberg, and V. Kozhevnikov, J. Phys.: Condens. Matter **17**, 3317 (2005).
[16] D. Akahoshi and Y. Ueda, J. Solid State Chem. **156**, 355 (2001).
[17] J. Rodríguez-Carvajal, Physica B **192**, 55 (1993).
[18] V. P. Plakhty, Y. P. Chernenkov, S. N. Barilo, A. Podlesnyak, E. Pomjakushina, E. V. Moskvin, and S. V. Gavrilov, Phys. Rev. B **71**, 214407 (2005).
[19] C. Frontera, J. G. García-Muñoz, A. Llobet, L. Mañosa, and M. A. G. Aranda, J. Solid State Chem. **171**, 349 (2003).